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# The Structure and Electron Density of Ethyleneimine Quinone

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The crystal structure of ethyleneimine quinone, 2,5-bis(ethyleneimino)-1,4-benzoquinone,  $C_6H_2O_2(NC_2H_4)_2$ , has been investigated at three different temperatures,  $300 \pm 5$ ,  $240 \pm 10$  and  $110 \pm 20$  °K. The crystal structures at the three temperatures are essentially the same. The crystal is triclinic, space group PT with Z=1. The three-membered ring of the ethyleneimino group is approximately a regular triangle with N-C=1·469, 1·475, C-C=1·498 Å, C-N-C=61·2, N-C-C=59·2 and 59·6°. Difference electron density maps through the three-membered ring revealed bonding electrons outside the triangle, in conformity with the theoretical prediction of the bent bond.

### Introduction

Triclinic prismatic along the c axis;

The three-membered rings of cyclopropyl, ethyleneimino and ethyleneoxido groups are typical examples of highly strained structures. Coulson & Moffit (1949) proposed the bent-bond model for cyclopropane on the basis of a valence bond treatment of the system; the bonding electrons are not centred on the C-C line but are displaced outside of the triangle, forming the bent bond. Recent SCF-LCAO-MO calculations have also revealed the bent-bond nature of these threemembered ring systems (Kochanski & Lehn, 1970; Bonaccorsi, Scrocco & Tomasi, 1970). The crystal structure analyses of 2,5-dimethyl-7,7-dicyanonorcaradiene by Fritchie (1966), and of cis-1,2,3-tricyanocyclopropane by Hartman & Hirshfeld (1966) have experimentally confirmed the validity of the bent-bond model by virtue of the electron distributions around the cyclopropyl group of the molecules.

Recently, the electron density distribution of the ethylene oxide ring was studied for tetracyanoethylene oxide by X-ray and neutron diffraction (Matthews & Stucky, 1970).

In order to investigate the electron distribution around an ethyleneimino group, the crystal structure analysis of ethyleneimine quinone, 2,5-bis(ethyleneimino)-1,4-benzoquinone,  $C_6H_2O_2(NC_2H_4)_2$ , was undertaken at room temperature and two lower temperatures (Ito & Sakurai, 1972). This compound seemed especially suitable for the present purpose, because preliminary experiments indicated that the crystal structure is simple (PI and Z=1), and no phase transition was observed throughout the observed temperature range. Difference electron density maps through the three-membered ring revealed bonding electrons outside the triangle, in accordance with the theoretical prediction of the bent bond.

## Experimental

Crystal data

2,5-Bis(ethyleneimino)-1,4-benzoquinone,  $C_6H_2O_2(NC_2H_4)_2$ ; F.W. 190.20,

	$300 \pm 5$ °K	240 ± 10 °K	$110 \pm 20^{\circ} K$
а	6·889 (7) Å	6·856 (4) Å	6·810 (4) Å
b	8.468 (6)	8.434 (3)	8.396 (3)
с	3.931 (3)	3.919 (3)	3.863 (2)
α	94·62 (7)°	94·10 (5)°	93·77 (4)°
β	100.13 (10)	99.66 (12)	9 <b>9</b> ·35 (11)
Ŷ	89.56 (8)	89.86 (4)	89.93 (6)
V	225.0 (3)	222.8 (2)	217·5 (2) Å <sup>3</sup>
$d_x$ (g cm <sup>-</sup>	<sup>-3</sup> ) 1·404	1.417	1.452

Z=1 from volume considerations.

Space group  $P\overline{1}$  from a statistical test.

Linear absorption coefficient for Mo K $\alpha$  radiation  $\mu = 1.22 \text{ cm}^{-1}$ .

Ethyleneimine quinone powder was prepared by dropwise addition of ethyleneimine to an ethanolic solution of *p*-benzoquinone (Gauss & Petersen, 1955). Orange prismatic crystals elongated along the *c* axis were obtained by recrystallization of the powder from benzene or acetone solutions.

The cell dimensions were determined from the sin  $\theta$  values of about thirty reflexions around the *c* axis, measured with an automatic diffractometer of equiinclination type, READ-1 (Sakurai, Ito & Iimura, 1970). The wavelength used was 0.71069 Å for Mo  $K\alpha$  radiation. The number of molecules per unit cell was found to be unity from a comparison of the cell volume of ethyleneimine quinone, 225.0 Å<sup>3</sup> at 300°K, with those of similar crystals; for example, V=414.8 Å<sup>3</sup> with Z=2 for tetrachloro-*p*-benzoquinone (Chu, Jeffrey & Sakurai, 1962). The N(z) test (Howells, Phillips & Rogers, 1950) clearly showed that the crystal is centric  $P\overline{1}$ .

## Low temperatures

The low temperatures were obtained with a Cryo-Tip refrigerator (Air Products & Chemicals). The refrigerator produces low temperatures by means of high-pressure nitrogen gas. The goniometer head of the diffractometer was specially designed to support the metal end of the refrigerator; the refrigerator was originally designed so that the vacuum shield end could be fixed to the goniometer head. This revision of installation minimized possible displacements of a sample crystal during measurements and allowed the use of a very thin glass vacuum shield with low background scattering of X-rays.

The temperature of a sample was measured with a copper-constantan thermocouple embedded in the copper block of the refrigerator. The measured temperature was calibrated with hexamine crystal as a standard. The lattice constants of hexamine given by Becka & Cruickshank (1963) were used for the calibration;  $a(298 \,^\circ\text{K}) = 7.021$  (9) and  $a(100 \,^\circ\text{K}) = 6.931$  (9) Å. It was found that the temperatures of the sample were higher than those detected by the thermocouple by 13 and 33° at 240 and 110°K respectively. The temperatures as detected by the thermocouple were kept constant within  $\pm 5^\circ$  during measurements.

## **Intensity measurements**

The intensities were measured with the automatic diffractometer READ-1 and Mo Ka radiation monochromated with a graphite monochromator of high mosaicity (Union Carbide). Two crystals were used for the measurements: one from benzene and another from acetone solutions were used at 300 and at 240 and 110°K, respectively. Both crystals were about 1 mm long along the c axis with cross sections of about  $0.25 \times 0.35$  mm. Reflexions around the c axis up to the 5th levels were explored; control measurements around the *a* axis at room temperature showed no significant deviations of interlevel scales from unity. The crystals were rotated in the  $\omega$ -scan mode with a scanning speed of 1° per min. The scan widths were so chosen as to be proportional to the peak widths (Ito, 1971). The diffracted X-rays were detected with a NaI scintillation counter and analysed with a pulse-height analyser. Strong diffraction beams were attenuated to within the linear range of the counter (below 4200 c.p.s.) by inserting zirconium foils with known attenuation factors.

Altogether 503, 773 and 895 independent reflexions were obtained at 300, 240 and 110 °K, respectively. These were corrected for Lorentz and polarization effects. Absorption corrections were not applied because they were negligible ( $\mu r \sim 0.02$ ). Extinction effects were found to be insignificant because no appreciable systematic discrepancies between  $F_o$  and  $F_c$  were observed during the refinement.

### **Determination of the structure**

The structure was first solved using the data collected at 300 °K. The space group  $P\bar{1}$  with Z=1 requires that the ethleneimine quinone molecule be located on the inversion centre. One half of the molecule,  $ONC_{s}H_{5}$ , constitutes the asymmetric unit of the cell. The exceptionally high  $F_{q}$  values of the 111 and 011 reflexions suggested that the quinone ring, C(1), C(2) and C(3), including O(1) and N(1) bonded to it, lies approximately on these planes. Therefore, a Patterson 111 section was calculated and approximate coordinates of the above atoms were easily obtained from analysis of the section. Coordinates of the two ethyleneimino carbons were obtained from a Fourier map. The structure was then refined by block-diagonal leastsquares calculations. After several cycles of isotropic and anisotropic refinement, the *R* value was 7.8%. At this stage, a difference electron density map clearly revealed all the hydrogen atoms. Several additional cycles of full-matrix least squares including the hydrogen atoms with isotropic temperature factors converged to the final *R* value of  $4\cdot1$ %.

The structures at 240 and 110°K could be refined starting from the results at 300°K. The final R values were 3.9 and 3.5%, respectively. No phase transition was observed within the observed temperature range.

# Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic temperature factors (Å<sup>2</sup>) with standard deviations

The *B* values for the non-hydrogen atoms are the equivalent isotropic temperature factors proposed by Hamilton (1959).

300° K	x/a	y/b	z/c	В
O(1)	1968 (4)	-2662 (3)	- 990 (8)	3.6
N(1)	1855 (4)	2565 (3)	4334 (8)	2.8
C(1)	1059 (5)	1288 (4)	2152 (9)	2.3
C(2)	1999 (5)	- 80 (4)	1676 (10)	2.6
C(3)	1080 (4)	-1435 (4)	-459 (10)	2.4
C(4)	2144 (5)	4110 (4)	3012 (11)	3.2
C(5)	3869 (5)	3121 (4)	4332 (11)	3.3
H(1)	3351 (47)	- 203 (38)	2648 (86)	3.2 (7)
H(2)	1815 (44)	4189 (36)	322 (82)	2.7 (7)
H(3)	1744 (47)	4991 (39)	4261 (88)	3.4 (8)
H(4)	4592 (51)	2538 (42)	2496 (94)	4.2 (8)
H(5)	4621 (47)	3419 (39)	6754 (88)	3.4 (8)
240° K				
O(1)	1983 (2)	- 2667 (2)	- 970 (4)	2.6
N(1)	1842 (2)	2571 (2)	4364 (4)	1.9
C(1)	1053 (3)	1289 (2)	2159 (4)	1.6
C(2)	2011 (3)	- 82 (2)	1694 (5)	1.9
C(3)	1083 (3)	- 1446 (2)	-465 (5)	1.7
C(4)	2134 (3)	4117 (2)	3007 (5)	2.2
C(5)	3863 (3)	3128 (2)	4374 (6)	2.5
H(1)	3381 (31)	-230 (26)	2711 (55)	2.3 (5)
H(2)	1759 (33)	4172 (27)	379 (58)	2.7 (5)
H(3)	1772 (32)	5044 (26)	4416 (57)	2.7 (5)
H(4)	4586 (33)	2565 (27)	2573 (58)	3.0 (5)
H(5)	4657 (34)	3378 (28)	6674 (61)	3.3 (5)
110° K				
O(1)	2007 (2)	-2680(1)	-946 (3)	1.1
N(1)	1817 (2)	2576 (2)	4397 (3)	0.8
C(1)	1041 (2)	1291 (2)	2181 (4)	0.7
C(2)	2020 (2)	- 87 (2)	1728 (4)	0.8
C(3)	1095 (2)	- 1450 (2)	-452 (4)	0.7
C(4)	2123 (2)	4138 (2)	3012 (4)	0.9
C(5)	3861 (2)	3139 (2)	4411 (4)	1.0
H(1)	3396 (28)	-215 (23)	2866 (50)	1.0 (4)
H(2)	1761 (30)	4180 (25)	389 (53)	1.4 (4)
H(3)	1744 (30)	5051 (24)	4354 (53)	1.4 (4)
H(4)	4603 (30)	2580 (25)	2709 (54)	1.6 (4)
H(5)	4640 (29)	3408 (24)	6793 (52)	1.3 (4)

Attempts to refine the anisotropic temperature factors of the hydrogen atoms turned out to be unsuccessful; the thermal ellipsoids of some hydrogens were extraordinarily elongated (at  $300^{\circ}$ K), or some led to nonpositive definiteness (at 240 and  $110^{\circ}$ K).

The final atomic coordinates and thermal parameters are given in Tables 1 and 2 respectively. The observed and calculated structure factors are compared in Table 3. The atomic scattering factors for the nonhydrogen atoms were taken from *International Tables* 

## Table 2. Thermal parameters with standard deviations

The thermal parameters refer to the expression:

	T =	$\exp\left[-10^{-4}.2\pi^{2}\right]$	$U_{11}h^2a^{*2}+\ldots+$	$2U_{12}hka^*b^*+\ldots$	.)].	
300° K	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
0(1)	352 (13)	310 (13)	670 (21)	84 (10)	49 (13)	- 74 (13)
N(1)	321 (14)	285 (14)	430 (21)	-43(11)	30 (14)	40 (14)
C(1)	282 (16)	285 (16)	332 (22)	-29(13)	53 (17)	59 (16)
C(2)	245 (16)	292 (16)	413 (24)	1 (13)	-23(16)	21 (17)
C(3)	277 (17)	263 (16)	377 (23)	9 (13)	72 (17)	25 (16)
C(4)	422 (20)	249 (16)	545 (28)	-41(14)	98 (20)	33 (18)
C(5)	326 (19)	404 (20)	521 (28)	-84 (15)	24 (19)	28 (20)
240° K						
O(1)	273 (7)	229 (7)	483 (9)	66 (6)	44 (6)	- 34 (6)
N(1)	248 (7)	211(7)	253 (8)	-43(6)	25 (6)	-13(6)
C(1)	208 (8)	201 (8)	210 (9)	-29(7)	38 (7)	11 (7)
C(2)	206 (8)	219 (8)	296 (9)	-1(7)	-3(7)	2 (7)
C(3)	218 (8)	204 (8)	241 (9)	-9(7)	40 (7)	15 (7)
C(4)	326 (10)	201 (9)	328 (10)	- 55 (7)	73 (8)	-7(7)
C(5)	248 (9)	298 (10)	374 (11)	-72 (8)	30 (8)	-8 (9)
110° K						
O(1)	126 (5)	103 (5)	179 (5)	23 (4)	25 (4)	-2(4)
N(1)	105 (5)	85 (5)	117 (6)	-17(4)	18 (4)	$\bar{2}(4)$
CÌÌ	87 (6)	107 (6)	81 (6)	-11(5)	19 (5)	5 (5)
C(2)	80 (6)	103 (6)	117 (6)	-6(5)	-4(5)	-6(5)
C(3)	94 (6)	85 (6)	95 (6)	-6(5)	25 (5)	6 (5)
C(4)	128 (6)	92 (6)	141 (7)	-17(5)	34 (5)	5 (5)
C(5)	103 (6)	114 (7)	144 (7)	-29(5)	9 (5)	-8(5)
		• •		• •	• •	• • •

Table 3. Observed and calculated structure factors ( $\times$  20) (a) 300 °K (503 reflexions)

K FO FC	K FO FC	K FU FC	K FU FC	K FO FC	K FU FC	K FO FC	K FO FC	K PO PC	K FO FC	* FO FC	K FO FC
	-10 33 28	- 70 81	-7 45 -49	-5 52 56				-4 104-114	1 6 2	2 223 229	-1 25 53
					-10 24 -25	<b>A F</b> 1	-7 = 2	-1 -10 -11	• •	62 - 59	0 34 -32
U K U		-3 90 81	-9 192 199	-4 190-148			•			4 30 43	1 207-202
	-8 137-145	-2 73 -71	+2	-3 227-223				-2 194 194	-0 148-145	6 30 43	1 207-202
1 149 146	-7 94-102	1 47 -50	-2 71 -69	-2 443 440	-6 14 -19	-7 58 -61	-2 26 61	-1 60 -61	-5 39 -38		2 26 29
2 381-373	-6 45 46	2 26 33	∪ 101 <b>-99</b>	-1 67 69	-6 77 81	-6 42 37	-3 26 22	0 19 15	-4 182 185	5 K 2	
3 171 148	-3 125-123	3 29 31	2 197 199	0 110 107	-5 308-299	-5 227 231	1 59 57	1 42 443	-3 149-149		1 5 3
. 144 144	-3 134 130		1 10 00		-4 172-169	-4 139 142	2 153 150	2 1 1 - 1 2 3	-2 295-287	-5 35 -41	
4 44 428	-2 134 130	4 134 136		2 107-100	- 1 22 2	-1 10 12	/ - / • / •		1 00 -00		-4 51 51
2 08 -62	-1 21 22	5 41 41	95 87	3 95 -93	- , ,	-, 20 1-		3 30 -36	-1 90 -90		
6 70 -70	0 557-548	6 41 - 34	6 64 -65	4 113-106	-2 112-116	-2 91 -90	-0 - 2	5 48 56	0 199 199	-2 26 -32	-5 01 03
7 267 267	1 163-152	7 31 -23		5 59 67	-1 324-318	-1 60 66		6 59 -65	1 188-176	-1 69 -77	-4 111-110
8 153 150	2 126 121		-4 5 1	7 24 21	0 97 - 98	0 73 71	-6 65 76		2 244-240	2 62 -64	-3 67 -68
• ••• •••	3 97 102	7 4 0			1 341 336	1 140-145	-5 71 80	-2 E 2	5 54 -44	5 55 -51	-2 29 -30
			-9 54 -54	,	3 620-614	2 172 176	-4 22 -14				0 20 24
	4 310-304					1 202 203	3 23 10	7			
	5 30 - 30	-6 32 36	-6 62 -62	-1 4 1	3 3-3-321	5 242 245		-0 +2 +1	9 87 -80		2 -8 -9
-9 10 -73	7 148-154	-5 27 -26	-7 21 -15		4 13 13	4 91 89	-2 38 -36	-> +2 -43			<b>.</b>
-8 96 95	8 92 -93	-4 92 -92	-6 90 88	-10 46 50	5 21 -23	5 111-110	-1 24 -20	-4 142-139	2 K 2	-4 30 33	-2 K 4
-7 56 59		-3 48 -50	-> 165-165	-9 126 127	6 27 24	ז וו ו	0 34 -44	-3 270 213		-2 64 -74	
-6 47 -47	4 K O	-2 27 23	-4 48 -40	-8 137 135	1 12 22	8 65 -60	1 119 117	-2 329 332	-9 36 -40	0 60 56	-1 66 -66
		-1 20 -22	-3 103 107		10 10 -42		2 141 147	-1 20A 19B	+7 23 10	2 104-103	AL- 61 0
-1 04 -01		- 20 -22	-2 140-140	120 125	+0 10 -64	5 6 1		72			
-3 43 -43	-1 33 -29	0 106-111	-2 103-103	-5 129 125			-	0 10 -14	-6 52 52	- 1 - 1	_
-2 249-246	-5 123 122	3 29 - 36	-1 301-296	17 -10	2 K 1			1 40 - 18	-> 140 153	-2 6 9	-1
-1 428 440	-4 176 175	5 40 -44	0 76 -69	-3 63 -60		-1 37 -49		2 140 149	-4 35 -31		
0 434 431	-3 31 34		1 201 195	-2 207 210	-9 87 -88	-5 91 46	-) 51 -53	5 169 183	-3 45 -52	-8 28 27	-4 16 -67
1 56 58	-2 144 140	8 K Q	2 103-105	-1 802 834	-8 138-145	-4 105 108	-4 66 64	6 156 158	-2 69 -63	-7 45 -42	-3 38 -34
2 245 251	-1 137-131		3 61 -62	0 628 693	-7 -01 -04	-3 38 -44	-3 38 -37	8 94 -88	-1 144-145	-6 28 -29	-2 27 24
3 375-372	0 144-120		156 140	1 505-532	-4 101-101	-2 73 -75	-2 181-190	9 43 46	1 58 48	-5 41 -45	-1 52 -47
5 21 10	0 146 127	-, 8, -0,				-1 133 124	-1 19 -41		3 33 30	- 110 109	0 /6 -73
	1 39 ~35			2 90 89	-4 84 87				1 13 10		
6 33 - 35	3 104 107	-8 K 1	0 91 +99	3 260 251	-3 67 70	0 62 -00	0 67 67	-1 K 2	4 26 23	-3 133 131	1 36 -35
7 163 160	4 35 32		/ 82 -87	4 153-147	-2 101-102	1 67 -69	1 23 22		7 35 32	-2 96 92	
8 133 127	5 127 126	-2 34 -36		5 37 -33	-1 421-413	2 161 160	2 67 -60	-10 33 34		0 90 -81	0 K 4
9 45 44	4 70 -73	0 17 -18	-3 K 1	A 214 215	0 148-148	4 45 45	3 87 87	-8 56 57	3 4 2	1 68 66	
10 84 -79				7 244 240	1 1 1 1 1 1 1	5 41 -52	<ul> <li>NR 33</li> </ul>	-5 34 -35		2 33 -34	-7 29 21
	1 63 - 10		-4 11	7		,	5 151-152	- 75 -75	-4 41 -10	2 33 36	
	9 41 -41		-1 00 00		2 137-144		6 33 -40	1 101 103			
		-/ 5 1		9 38 - 36	3 195-121	0 K 1	0 33 -40	-3 103 103	-0 183 197	-1 4 3	
	3 K O		-6 51 -50	10 34 36	4 96 -96			-2 324 314	-> 112 119		1
-9 28 23		-5 96 97	-5 279-278		5 101 96	-5 84 -82	1 2	-1 287 276	-4 42 -54	-9 50 39	
-8 100 -98	-7 31 35	-> 36 -+2	-" 52 53	0 K 1	6 37 - 20	-4 46 -45		0 243-230	-3 48 58	-8 46 -44	-5 46 -41
-7 171-181	-6 66 -68	-2 45 42	-3 17 -22		7 183-188	-1 86 -98	-6 22 15	2 99 102	-1 23 -26	-7 00 -00	-2 63 -51
-6 169 168	-1 11 10	-1 -0 -14	-2 94 -94	-a 133 136	8 60 60	0 63 -64	-6 137-147	4 35 27	0 20 -17	-6 28 -28	-1 96 90
-5 51 -10	-4 107 108		-1 204-194	-7 30 -41		1 44 72	-3 60 -62	6 169 182	1 116 122		0 105 102
-4 143-174	- 191 190	0 23 -31	0 114-117	- 83 -		3 66 74	-4 117 122	4 45 -44	2 244 247		
	-3 2 - 3 2 - 1	5 51 53				2 28 -63	-1 141-1-1	• • • • • • •			2 F A
-3 +2 -34	•Z /2 =19		1 196 191	-7 31 39		3 32 -28	-3 138-138		3 61 64	-3 24 -34	
-2 101 92	-1 116-114	-6 K 1	4 167-159	-4 120-112	-8 40 -44	4 30 28	-6 +20-133	0 K Z	+-	-2 44 46	· · · ·
-1 80 -80	0 203 205		3 206-198	-3 145-150	-7 30 -31	5 40 -34	0 41 44		5 49 -48	-1 37 -29	-1 90 83
0 526-518	1 72 -74	-5 169 175	4 50 -48	-2 91 94	-5 194 199		1 90 -93	-10 63 -66	6 34 34	0 59 -61	0 75 80
1 186 190	2 73 -75	- 07 04	5 83 84	-1 801 6-1	-3 24 -21	7 5 1	2 145-140	-6 64 -38		1 87 -84	
2 16 -17	1 170 166	71 90	6 65 .66	0 62 73	-2 78 85		3 51 54	-5 158-173	<b>4 K 2</b>	2 #3=100	
3 301-243	5 110 100	-1 37 37	/ 107-201	1 21 2 21 1	111-112		5 79	-4 63 61		. 35,100	
3 301-272	- 251 252	1 113-114			0 113-112				-1		
4 132-118	5 47 51	2 179 170	0 48 4Y	2 108 107	1 37 62	-1 63 -68	0 44 - 45		-0 70 77	U K J	
5 153-149	6 95 -89	3 229 230		3 113-104	2 135 142	2 63 -65	1 21 -22	-1 33 -34	-> 10 13		
6 87 86	7 41 36	4 26 -28	-2 K 1	6 166 160	3 29 27	3 68 -66		0 48 42	-3 51 -54	-6 /3 -63	
10 28 -23				7 191 191	4 20 17		-3 K 2	1 77 -80	-2 28 30	-5 72 67	
	6 5 0	/ -/ -43	-9 128 126	+0 +0 -39	5 81 74	-8 5 2		2 303-324	-1 61 58	-4 25 -23	
3 8 0	• • •	-1 1 1			7 39 -53	- ·· •	-0 82 49	9 75 -72	0 119-127	-3 190-147	
- x v		-2 4 1		1				1 12 -14	1 120 127	-2 20 -201	
	-6 -5 -60		-0 03 -03		8 48 42	** 78 ***				-4 -7 -64	

Table 3 (cont.) (b) 240°K (773 reflexions)

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c} x & FO & FC \\ -2 & 33 & 54 \\ -3 & 53 & -59 \\ -5 & 53 & -59 \\ -6 & x & 1 \\ -8 & 56 & -52 \\ -6 & 31 & 31 \\ -8 & 56 & -52 \\ -6 & 31 & 31 \\ -8 & 70 & 205 \\ -1 & 49 & 453 \\ 2 & 200 & 2052 \\ -1 & 49 & 453 \\ 2 & 200 & 2052 \\ -1 & 49 & 453 \\ 2 & 200 & 2052 \\ -1 & 49 & 453 \\ -2 & 60 & 205 \\ -3 & 200 & 205 \\ -5 & x & 1 \\ -9 & 73 & -77 \\ -5 & 56 & -57 \\ -5 & 11 \\ -9 & 73 & -77 \\ -5 & 56 & -57 \\ -5 & 173 & 171 \\ -1 & 73 & -77 \\ -5 & 56 & -57 \\ -5 & 11 \\ -9 & 73 & -77 \\ -5 & 56 & -57 \\ -5 & 10 & -187 \\ -5 & 56 & -57 \\ -5 & 10 & -187 \\ -5 & 56 & -57 \\ -5 & 10 & -187 \\ -5 & 56 & -57 \\ -5 & 10 & -187 \\ -5 & 56 & -57 \\ -5 & 10 & -187 \\ -5 & 57 & -57 \\ -5 & 10 & -187 \\ -$	$ \begin{array}{c} {\tt K} & {\tt FO} & {\tt FC} \\ {\tt 2} & {\tt 164-163} \\ {\tt 3} & {\tt 164-163} \\ {\tt 5} & {\tt 164-163} \\ {\tt 7} & {\tt 2} & {\tt 364} \\ {\tt 7} & {\tt 8} & {\tt 7} \\ {\tt 7} & {\tt 8} & {\tt 7} \\ {\tt 7} & {\tt 8} & {\tt 7} \\ {\tt 7} & {\tt 8} & {\tt 7} \\ {\tt 7} & {\tt 8} & {\tt 7} \\ {\tt 7} & {\tt 8} & {\tt 7} \\ {\tt 7} & {\tt 7} & {\tt 164-163} \\ {\tt 7} & {\tt 7} \\ {\tt 7} & {\tt 164-163} \\ {\tt 7} & {\tt 7} \\ {\tt 7} & {\tt 164-163} \\ {\tt 7} & {\tt 7} \\ {\tt 7} & {\tt 164-163} \\ {\tt 7} & {\tt 1164-163} \\ {\tt 7} & {\tt 1164-164-164-164-164-164-164-164-164-164$	$ \begin{array}{c} k & fO & fC \\ 6 & 50 & -230 \\ 7 & 203 & -230 \\ 10 & 66 & -84 \\ 11 & 90 & -84 \\ 11 & 90 & -84 \\ 3 & \kappa & 1 \\ -8 & 48 & -50 \\ -7 & 32 & -81 \\ -7 & 32 & -81 \\ -7 & 32 & -21 \\ -8 & 68 & -50 \\ -7 & 30 & -12 \\ -7 & -12 & -27 \\ -7 & -7 & -77 \\ -7 & -77 $	$ \begin{array}{c} {\tt k} {\tt FO} {\tt FC} \\ {\tt 5} {\tt 76} {\tt 72} \\ {\tt 9} {\tt k} {\tt 1} \\ {\tt -1} {\tt 96} {\tt 8} \\ {\tt -9} {\tt k} {\tt 2} \\ {\tt 28} {\tt -67} \\ {\tt -6} {\tt k} {\tt 2} \\ {\tt -6} {\tt 59} {\tt 60} \\ {\tt 1} {\tt 36} {\tt 43} \\ {\tt -7} {\tt k} {\tt 2} \\ {\tt -6} {\tt 59} {\tt 60} \\ {\tt -1} {\tt 35} {\tt -37} \\ {\tt 2100} {\tt 112} \\ {\tt -6} {\tt k} {\tt 2} \\ {\tt 100} {\tt 191} \\ {\tt -5} {\tt k} {\tt 2} \\ {\tt 100} {\tt 191} \\ {\tt -5} {\tt k} {\tt 2} \\ {\tt -6} {\tt 50} {\tt -89} \\ {\tt -5} {\tt 50} {\tt -89} \\ {\tt -2} {\tt 218-216} \\ {\tt -1} {\tt 33} {\tt -33} \\ {\tt 33} {\tt -33} \end{array} $	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	K         FO         FC           3         K         2           -10         47         52           -8         61         -55           -10         22         22           -10         23         24           -11         30         -26           30         24         23           12         24         23           3         64         64           60         -57         5           5         62         63           61         64         463           6         40         5           5         62         62           7         62         63           6         44         403           6         44         403           7         62         62           7         70         62           7         70         70           7         70         70           7         70         70           7         70         70           7         70         70           7         70         70	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c} {\tt K} & {\tt FO} & {\tt FO} \\ {\tt 4} & {\tt 32} & {\tt 33} \\ {\tt 6} & {\tt 33} & {\tt 37} & {\tt -32} \\ {\tt 9} & {\tt 27} & {\tt -32} \\ {\tt 9} & {\tt 27} & {\tt -32} \\ {\tt 0} & {\tt K} & {\tt 3} \\ {\tt -6} & {\tt 79} & {\tt 78} & {\tt 86} \\ {\tt -4} & {\tt 29} & {\tt 270} \\ {\tt -4} & {\tt 29} & {\tt 270} \\ {\tt -4} & {\tt 29} & {\tt 270} \\ {\tt -20} & {\tt 233} & {\tt 2277} \\ {\tt 0} & {\tt 00} & {\tt 233} & {\tt 2277} \\ {\tt 0} & {\tt 00} & {\tt 233} & {\tt 2277} \\ {\tt 1} & {\tt 222} & {\tt 240} \\ {\tt 1222} & {\tt 240} \\ {\tt 1222} & {\tt 4168} & {\tt 181} \\ {\tt 1} & {\tt 86} & {\tt 86} & {\tt 171} \\ {\tt 868} & {\tt 861} & {\tt 171} \\ {\tt 868} & {\tt 868} & {\tt 171} \\ {\tt 868} & {\tt 868} & {\tt 171} \\ {\tt 868} & {\tt 868} & {\tt 171} \\ {\tt 868} & {\tt 861} & {\tt 171} \\ {\tt 868} & {\tt 868} & {\tt 171} \\ {\tt 7} & {\tt 868} & {\tt 737} \\ {\tt 1} & {\tt 86} & {\tt 353} \\ {\tt 1} & {\tt 35} & {\tt 55} & {\tt 557} \\ {\tt 7} & {\tt 590} & {\tt 90} \\ {\tt 502} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 590} & {\tt 750} \\ {\tt 7} & {\tt 70} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {\tt 700} & {\tt 700} \\ {\tt 7} & {$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
3 306-302 4 139-128 5 163-156 6 94 93 8 46 -49 11 38 -33 3 K 0 -10 46 41 -9 47 47 -8 154-161 -7 106-119 -6 35 46	8 K 0 -6 42 43 -4 79 -77 -3 109-103 4 146-146 5 43 -52 6 64 66 9 K 0 -3 72 -62 -2 37 30 -1 44 44	1 213 213 2 121-118 3 62 -63 4 169 174 5 71 -80 6 104-111 7 92 -99 9 59 57 -3 K 1 -7 106 105 -6 47 -54 5 123-202	120-120 6 181 187 7 207 211 9 34 -27 10 50 -49 11 40 44 1 K 1 -9 51 -58 -8 90 -48 -8 90 -48 -6 86 91 -5 326-316 -4 179-177 -6 187 -6 187 -6 187 -6 187 -7 207 211 -7 207 211 -8 -27 -8 -27	-5 102 103 -4 116 122 -3 42 -67 -2 89 -94 -1 146 134 0 63 -76 1 79 -77 2 169 174 3 156 180 4 55 55 5 68 -67 9 56 52	2 72 -79 3 106 107 4 38 36 5 188-191 6 39 -42 -4 K 2 -10 40 -45 -6 173-175 -5 78 -73 -4 144 142 -3 168-164 -2 190-145		6 K 2 -6 135-129 -5 93 -92 -6 49 49 -2 77 -63 0 76 76 1 106-105 2 128-126 4 32 -25	-10 111 115 -5 87 -83 -4 109 108 -3 298 293 3 30 -26 4 161 161 5 108 106 7 38 -38 9 37 41 -2 K 3 -8 36 32	-3 82 90 -2 115-122 0 141 147 1 198 196 2 63 67 3 59 -61 5 32 -36 8 44 44 3 K 3 -7 76 77 -5 32 77 -5 32 -26	-2 K 4 -8 89 -87 -2 27 28 -1 93 -91 1 27 -24 3 106 107 7 31 -45 -1 K 4	0 53 -54 1 40 46 2 62 72 3 77 78 -3 K 5 -1 76 -80 3 60 63 -2 K 5 -2 K 5 -2 K 5 -2 40 -40 -1 54 -65
-3 128-128 -2 131 133 -1 66 72 0 557-558 1 171-159 2 131 129 3 107 110 4 330-324 6 174 177 7 170-172 8 106-109 11 73 -69 4 K 0	0 47 47 1 38 42 2 37 36 3 46 -45 -9 K 1 -4 39 -42 -3 66 62 0 45 41 2 99 -95 3 89 -83 -8 K 1	-* 57 52 -3 26 -24 -2 99 -99 -1 205-205 0 115-113 1 159 157 2 178-173 3 217-203 4 54 -52 5 88 87 7 0 -85 7 224-230 8 70 70 8 70 70	-2 118-123 -1 337-332 U 96 -97 1 351 349 2 449-400 3 362-448 4 78 80 6 34 33 9 32 -30 10 85 -77 2 K 1 -11 53 54	-5 102 -97 -4 53 -56 -1 95-112 0 75 -77 1 89 88 2 75 -74 5 45 -44 7 51 -50 7 K 1 -7 66 67 -5 145-135	0 44 48 1 106-107 2 164-157 5 89 -96 6 114-112 8 70 69 9 76 -65 -3 K 2 -10 68 65 -9 105 107 -7 33 -30 -6 61 -62	-5 48 -47 -5 206 214 -3 164-161 -2 313-308 -1 95 -93 0 216 219 1 195-186 2 271-266 3 86 83 5 64 -66 6 109-117 9 115-111 10 68 -66	7 K 2 -6 49 -57 -3 38 40 -2 64 57 1 37 -84 2 63 -54 3 54 -61 4 44 45 3 42 39 8 K 2	-6 28 -27 -5 51 -56 -6 119 116 -3 178 176 -2 112 105 0 97 -97 1 87 87 2 46 -51 3 43 -46 4 229 223 5 156 156 7 70 -73 -1 K 3	1 235 243 2 56 53 3 85 -86 8 156 147 4 K 3 -1 56 -53 0 36 40 1 43 44 2 60 -56 4 37 -36 5 58 -58	-4 99 -97 -3 36 -40 0 92-100 1 42 -41 2 77 78 3 53 -58 4 96 -99 5 69 69 7 87 -82 0 K 4 -8 39 45 -6 40 34	-1 K 5 -5 39 -46 2 50 -52 3 57 -60 4 36 36 0 K 5 -1 114 120 2 32 -25 1 K 5
-6 104-108 -5 125 126 -4 186 190 -3 33 39 -2 154 150 -1 138-132 0 145-132 1 38 -36 3 112 116 4 61 59 5 134 136 6 80 -81 7 67 -77	-6 36 -33 -5 64 -63 -4 39 40 0 41 -48 2 62 -62 3 84 -83 -7 K 1 -7 47 -46 -5 114 120 -4 37 39 -3 51 -52	11 40 -32 -2 K 1 -11 52 -57 -9 149 154 -8 105 104 -5 36 -60 -5 63 64 -4 160-161 -3 242-233 -2 475 461 -1 77 70 0 110 107	-9 100-102 -8 163-170 -7 93 90 -5 194-190 -4 83 87 -3 66 74 -2 98 -93 -1 430-42 0 155-155 1 186 190 2 157-142 3 173-168 4 104-104 5 115 112	-• 73 -69 -1 67 -77 2 73 -71 3 76 -76 4 89 -93 7 82 -88 8 K 1 -4 62 -58 -2 82 77 -1 43 38 0 41 37 3 106 -99	-* 128-128 -3 71 68 -2 229 218 -1 77 -80 1 50 -45 2 148-134 3 53 -59 5 54 57 6 66 -76 9 78 -66 -2 K 2 -10 179 177	2 K 2 -9 43 -49 -6 68 64 -5 166 167 -3 46 -49 -2 67 -59 -1 166-186 0 46 52 1 76 79 2 84 83 6 158-170 7 51 50 9 40 -42	-3 63 68 -2 84 80 -1 83 74 -8 K 3 -2 69 -70 0 91 98 1 57 60 -7 K 3 -6 67 64 -2 36 -37	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 K 3 -7 57 -57 -6 98 -95 -3 76 -95 -3 76 -95 -1 40 35 1 164-161 3 45 41 4 98 -92 6 K 3 0 58 -56 1 78 -75	-4 126-127 1 33 35 3 106-111 1 K 4 -8 104 97 -7 72 76 -5 58 -53 -2 74 -77 -1 128 129 0 132 137 1 36 32 2 34 -**	-3 46 -40 -2 99 100 -1 97 98



Fig. 1. Structure of ethleneimine quinone viewed down the caxis. c is out of the plane of the paper.

for X-ray Crystallography (1962). Those for a free hydrogen atom listed in the Table were found to be inappropriate in the present case, because the B values of the hydrogen atoms were systematically smaller than those of the carbon atoms to which they are bonded; moreover, all of them became negative at 110°K. Therefore, the atomic scattering factors for a hydrogen atom in a hydrogen molecule (Stewart, Davidson & Simpson, 1965) were used with better results. The average difference between the two corresponding B values was about 2.0 Å<sup>2</sup>.

## **Results and discussion**

# Crystal structure

The crystal structures of ethyleneimine quinone at 300, 240 and 110°K are essentially the same. The structure viewed down the c and a axes is shown in Figs. 1 and 2, respectively. The molecules lie approximately on

# Table 3 (cont.) (c) 110°K (895 reflexions)

К FO FC 0 К 0	K FO FC -7 66 75 -6 95 -90	K FO FC -6 K 1	K FQ FC	K FO FC -1 293-284 0 127-124	к FO FC 8 к 2	K FO FC 0 96 -99 1 84 -77 2 210 209	K FO FC -3 81 82 1 140 143 2 343 352	K FO FC -3 153-154 -2 42 -44 -1 52 55	K FO FC -2 28 -21 -1 103 104 0 75 -78	K FO FC -6 K 4	K FO FC -4 67 69 -3 105-104 -1 141 145
1 135 134 2 380-377 3 184 175 4 180 175 5 89 -89	-3 335 344 -2 75 -79 -1 173-173 0 261 257	-6 48 47 -5 273 280 -4 116 120 -1 63 57 1 158-160	-9 203 203 -8 180 182 -7 41 39 -6 70 -67 -5 153 155	2 163 173 3 36 39 5 100 96 6 172-188 7 63 -65	-6 103 107 -5 61 68 -4 78 -75 -2 51 51 -1 138-141	3 109-109 4 57 -53 5 270 268 6 231 241 8 155-155	3 81 83 4 67 -72 5 60 -71 6 75 71 8 66 -61	3 63 63 4 153-150 5 134-136 6 97 91 7 39 35	1 310-297 2 60 65 3 110 107 4 223-231 8 124-121	-3 60 -53 -2 89 81 -1 98 -92 0 71 -74 3 154-151	0 152 149 1 121 125 2 89 -87 4 37 37
6 70 -67 7 348 354 8 182 183 11 48 -45	2 103-104 3 194 195 4 337 340 5 65 75	2 280 277 3 302 310 4 75 -79 5 55 -52	-4 76 -63 -3 83 -81 -2 229 222 -1 853 883	8 40 38 4 K 1	1 68 72 -7 K 2	9 114 114 -1 K 2	9 223 216 4 K 2	-5 K 3 -8 59 -56 -7 66 -76	9 113-105 1 K 3 -10 52 -50	4 148-144 -5 K 4 -3 91 92	3 K 4 -5 42 -47 -4 70 -71 -1 56 -51
1 K 0 -9 117-124 -8 119 122	6 134-135 7 62 62 6 K O	7 60 59 8 104-101 9 72 72	1 562-578 2 130 120 3 284 278 4 188-177	-5 299 302 -4 193 197 -3 35 28 -2 126-130	-6 173 177 -5 109 107 -4 45 -49 -3 58 58	-9 43 42 -8 108 102 -7 108-111 -4 106-105	-6 133 134 -5 119 121 -3 91 -98 -1 110 100	-6 116-113 -5 78 78 -3 238-238 -2 54 54	-8 70 63 -7 58 51 -6 68 65 -5 127 130	-1 98-103 1 50 -44 3 43 -46	0 78 83 2 81 -79 4 71 -74
-7 75 81 -6 73 -72 -4 127-122 -3 106-111 -2 248-253	-9 111-107 -6 80 -78 -4 95 103 -3 128 129 -2 102-106	-5 K 1 -9 112-119 -7 60 -65 -5 205 206	5 37 -31 6 286 297 7 305 311 8 123-130 10 60 61	-1 82 81 0 108 106 1 215-214 2 205 212 3 372 381	$\begin{array}{c} -1 & 54 & -54 \\ 1 & 104 & 103 \\ 2 & 265 & 264 \\ 4 & 95 & -96 \\ 5 & 70 & 71 \end{array}$	-2 367 348 -1 331 316 0 287-283 2 118 117	$ \begin{array}{r} 1 & 154 & 161 \\ 2 & 317 & 323 \\ 4 & 94 & -90 \\ 6 & 65 & 72 \end{array} $	0 124-122 1 136-135 2 67 69 3 33 33	-3 77 -76 -2 60 -53 0 67 77 2 64 60	-7 48 -53 -6 61 -54 -5 76 81	-4 78 -87 -3 37 -37 -1 54 -49
-1 415 428 0 420 433 1 69 66 2 245 252 3 399-399	1 63 -66 2 37 39 4 205 209 5 71 79	-4 65 61 -2 99 -98 0 123-121 2 263 273 3 89 88	0 K 1 -8 197 197 -7 42 -41	4 114 119 5 160-162 7 122 117 8 114-113 9 73 66	7 49 -43 -6 K 2 -8 36 36	3 181-178 4 67 63 5 244 250 6 233 242 8 49 -45	7 95 -88 8 75 62 9 196 185 5 K 2	4 235-241 5 53 -51 -4 K 3	3 56 -59 5 86 -98 6 76 -81 7 113 116 8 65 -64	-3 89 90 -2 135-136 -1 92 95 1 109-111	0 118-120 1 96 -91 2 93 90 3 81 -84 4 159-151
4 32 33 5 28 28 6 42 -43 7 201 200	7 56 -55 9 44 51 7 K 0	4 112 112 5 36 -31 6 82 -88 9 87 87	-6 128-126 -5 63 71 -4 128-118 -3 157-161	10 174 166 5 K 1	-6 127 120 -5 142 142 -3 33 -33 -2 48 -47	10 43 -42 0 K 2	-7 40 -37 -5 94 -91 -1 112-118	-7 56 -51 -6 73 -72 -4 40 -43 -3 135 137 -2 50 52	9 56 -50 2 K 3 -9 115-110	2 50 42 3 153 153 4 128 131 5 61 -62	5 K 4
9 71 66 10 152-150 2 K 0	-7 148-136 -6 73 71 -4 149-145 -3 93 -96	-4 K 1 -9 106-108 -8 93 -96	-1 806 842 0 57 58 1 218-216 2 113 109	-8 61 67 -7 81 -79 -6 40 -39 -5 126 124	1 200 197 2 236 240 3 49 -56 6 35 -28	-7 51 -54 -6 90 -83 -5 202-195 -4 97 97	2 126-127 3 48 44 5 117-109 6 66 -63	-1 107-109 1 98 -91 2 59 -55 4 32 36	-8 36 34 -7 213 211 -6 203 204 -5 82 -83	-3 K 4 -7 102-100 -5 82 88	0 132-132 -5 K 5
-11 90 -73 -9 54 55 -8 120-122 -7 254-274	0 169-180 3 52 -60 5 78 -72 7 45 -49	-6 105 106 -5 234-239 -4 36 -36 -3 254 252 -2 228-224	3 139-133 6 207 217 7 237 242 9 38 -37 10 70 -70	-4 145 150 -3 48 -50 -2 122-128 -1 171 160 0 71 -86	6 73 75 -5 K 2 -5 77 -73	-3 27 -30 -2 140-144 +1 25 -27 0 70 73 1 118-112	8 48 46 6 K 2 -7 89 80	6 69 -77 7 52 34 8 97 -87 -3 K 3	-3 141 145 -2 163-167 0 196 195 1 240 235 2 68 76	-3 31 34 0 69 -73 1 30 30 3 177 175	-1 /3 eV 0 91 -93 -4 K 5
-6 205 199 -4 428-426 -3 58 -49 -2 101 93 -1 61 -63	8 K 0 -6 82 77 -5 40 -33 -4 94 -93	-1 348-339 0 53 -48 1 236 241 2 153-151 3 62 -58	11 79 79 1 K 1 -11 42 41	1 100 -98 2 188 193 3 182 191 4 77 83 5 91 -87	-4 112 113 -3 76 -76 -2 276-274 0 104 107 2 102-106	2 420-413 3 37 38 4 120 114 5 90 -86 6 66 71	-6 204-199 -5 157-152 -4 85 82 -2 101-109 -1 43 -47	-9 67 -65 -7 64 67 -6 44 -43 -5 121-120	3 67 - 75 8 89 79 3 K 3	4 210 209 6 36 -48 -2 K 4	-4 56 67 -3 58 -58 -2 57 53 0 94 -95 1 87 91
0 529-534 1 183 186 3 313-310 4 150-139 5 179-172	-3 174-164 -1 55 52 0 41 -49 1 43 -38 4 224-223	4 205 206 5 110-116 6 120-125 7 116-122 9 79 82	-10 35 -31 -9 82 -79 -8 119-125 -6 116 124	9 66 64 6 K 1 -8 70 -65	3 151 151 4 37 34 5 257-264 8 56 51	8 39 -32 9 140-141 1 K 2	0 120 115 1 138-138 2 182-176 4 43 -35 6 111-105	-4 161 157 -3 393 384 -1 27 -20 0 42 47 4 221 224	-9 67 -62 -7 99 98 -6 117 115 -5 39 -39 1 316 323	-8 174-166 -5 43 -46 -3 28 32 -2 39 38 -1 150-149	2 123 124 -3 K 5 -4 44 50
6 108 104 8 63 -56 11 58 -53	5 75 -84 6 115 112 9 K 0	-3 K 1	-4 210-206 -3 273 272 -2 131-134 -1 362-354	-6 49 45 -5 139-138 -4 90 -90 -1 123-142	-4 K 2 -10 69 -69 -6 233-236	-10 122-126 -9 139-142 -7 115 122 -6 203-199	7 K 2	5 141 137 7 66 -63 9 75 77	2 72 75 3 125-122 8 246 239	0 60 -63 2 34 -33 3 136 139 7 85 -78	-2 59 -60 -1 127-128 0 35 34 3 114 118
-10 64 66 -9 63 66 -8 193-204	-3 116-109 -2 49 54 -1 63 61 0 75 77	-9 49 -50 -8 38 -42 -7 124 127 -6 56 -60 -5 358-353	0 96 -99 1 368 365 2 472-467 3 376-361 4 87 88	$ \begin{array}{c} 1 & 116 & 118 \\ 2 & 104 - 106 \\ 3 & 36 & -45 \\ 4 & 54 & 51 \\ \end{array} $	-4 185 183 -3 199-198 -2 170-169 0 47 51	-4 261 264 -3 180-178 -2 353-347 -1 105-104	-2 99 98 0 42 41 1 52 -51 2 75 -72	-7 70 -73 -5 73 -71 -4 124 124	-8 68 -66 -3 87 -93 -1 76 -78	-1 K 4 -8 83 -82 -4 162-158	-2 K 5 -3 52 -54 -2 68 -70
-7 129-144 -6 62 55 -3 143-140 -2 132 133 -1 99 101	1 65 63 2 66 64 3 56 -53 -9 5 1	-4 64 57 -2 105-101 -1 217-216 0 115-113 1 164 160	6 56 31 9 52 -48 10 97 -97 2 K 1	5 56 -60 6 59 -59 7 79 -72 7 K 1	1 137-139 2 189-183 3 73 83 5 111-116 6 142-142	0 248 248 1 209-200 2 297-288 3 100 95 5 78 -79	5 76 75 6 K 2	$\begin{array}{r} -3 & 214 & 211 \\ -2 & 143 & 133 \\ 0 & 131 - 127 \\ 1 & 121 & 121 \\ 2 & 67 & -61 \end{array}$	0 35 39 1 43 48 2 76 -76 3 37 42 4 70 -67	-3 69 -64 -2 85 85 -1 81 -98 0 140-150 1 50 -48	-1 106-112 3 101 -98 -1 K 5
0 584-586 1 189-178 2 143 142 3 124 128 4 377-369	-4 49 -52 -3 109 107 -2 83 -86 0 71 69	2 207-201 3 231-215 4 52 -56 5 106 101 6 103-115	-11 88 88 -9 129-134 -8 213-225 -7 117 113	-7 126 120 -5 204-200 -4 103 -97 -1 104-103	7 33 -29 8 92 95 9 110-106 -3 K 2	6 134-148 8 58 62 9 167-154 10 108-107	-2 122 118 -1 127 129 1 53 -44	3 63 -60 4 288 290 5 200 204 7 99-100 8 68 76	5 88 -86 7 42 41 5 K 3	2 121 118 3 116-113 4 150-152 5 124 121 6 50 -51	-5 79 -80 +4 85 -93 -3 77 72 0 35 37 2 85 +90
6 211 209 7 203-211 8 138-143 11 121-119	2 168-165 3 126-122 -8 K 1	7 276-285 8 110 109 10 121-113	-5 219-217 -4 98 98 -3 76 78 -2 86 -83	2 91 -89 3 106-104 4 139-143 5 68 70	-10 109 103 -9 156 155 -6 61 -57	2 K 2 -9 49 -56 -7 34 36	-8 K 3 -3 51 53 -2 122-124 0 148 175	-1 K 3	-7 83 -80 -6 177-175 -5 47 44 -4 34 33 -3 126-130	7 149-144 0 K 4	3 106-108 0 K 5
4 K 0 -6 134-136 -5 133 137	-5 99-101 -4 64 60 -3 55 -56 -2 58 -63	-11 77 -81 -10 39 -39 -9 219 221	0 182-180 1 201 206 2 150-137 3 187-180	8 K 1 -4 94 -91 -2 129 125	-3 108 104 -2 264 257 -1 107-109 1 51 -45	-5 210 208 -4 57 -58 -3 44 -45 -2 53 -45	1 86 88 2 49 44 3 67 -60	-8 98 -90 -7 130-122 -5 34 -34 -3 79 -84	-1 51 58 1 251-248 3 63 68 4 145-143	-6 57 53 -4 187-192 1 45 38 3 144-148	-1 217 217 1 K 5
-3 45 47 -2 178 160 -1 153-145 0 154-141	2 108-104 3 109-108 -7 K 1	-6 67 -59 -5 78 85 -4 177-177 -3 259-252	5 139 133 6 59 -67 7 257-268 8 67 69	$\begin{array}{c} -1 & 51 & 53 \\ 0 & 55 & 61 \\ 3 & 149 - 147 \\ 4 & 55 & -46 \\ 5 & 126 & 121 \end{array}$	3 69 -71 5 65 67 6 95-100 7 47 56	0 50 56 1 103 108 2 102 98 4 39 34	-6 110 111 -4 37 -44 -3 37 -37	-1 28 -24 0 104-107 1 135-134 2 129-133	6 K 3	1 K 4 -6 168 178 -7 122 123	-2 169 174 -1 154 164 2 K 5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-8 59 -67 -7 69 -73 -6 55 56 -5 173 175	-2 514 500 -1 85 78 0 109 108 2 176-172 3 110-101	10 129-128 11 137-137 3 K 1	9 K 1 0 176 168	-2 K 2 -10 276 277	6 199-217 7 68 69 8 41 40 9 60 -58	-2 36 -41 -1 40 40 0 76 77 1 219 219 2 37 37	5 152 150 6 85 81 7 46 -45 8 94 -92 9 87 -84	-3 62 62 -2 61 69 0 69 -64 1 116-113 4 65 66	-5 /4 -74 -4 61 62 -2 120-128 -1 203 210 0 196 199	-2 41 32 0 78 79 1 42 -44
7 75 -82 9 74 -76 5 K 0	-3 84 -82 -2 87 85 -1 74 -83 0 47 -50 3 83 87	4 119-110 5 70 74 7 48 55 9 121-119 11 51	-11 56 54 -8 56 -54 -7 61 -54 -5 262 268	-9 K 2 -3 128-132 -2 42 -42 0 48 -47	-9 127 125 -6 85 88 -5 52 -50 -4 193-189 -3 355 343	3 K 2 -10 113 103 -8 87 -89 -6 292 204	3 90 -94 4 60 54 -6 к 3	0 K 3	-7 K 4 -2 39 38 0 55 53	2 47 -43 5 79 -82 6 97 97 2 K 4	
-10 83 77	6 42 -44	-1 K 1	-3 34 -37	1 87 -86 2 106-106	-2 418 407	-5 181 181 -4 85 -92	-6 80 81 -4 41 -40	-5 127 123 -3 304-307	2 54 -57	-7 71 69	

the  $(\overline{11}1)$  planes forming molecular sheets. These sheets are stacked along the *c* axis. The intermolecular interactions between the adjacent sheets as well as within a sheet are van der Waals contacts.

The closest intermolecular distances are summarized in Table 4. These values can be regarded as normal compared with the sums of the van der Waals radii of the atoms;  $O \cdots C = 3 \cdot 4$ ,  $N \cdots C = 3 \cdot 5$ ,  $C \cdots C = 4 \cdot 0$ ,  $O \cdots H$  $= 2 \cdot 6$ ,  $N \cdots H = 2 \cdot 7$ ,  $C \cdots H = 3 \cdot 2$  and  $H \cdots H = 2 \cdot 4$  Å (Pauling, 1960). It should be noted that intermolecular distances decrease with decreasing temperatures probably because of the decreasing thermal vibrations of the molecules (see the last column of Table 4).



Fig. 2. Structure of ethyleneimine quinone viewed down the *a* axis. **a** is out of the plane of the paper.

# Table 4. Intermolecular van der Waals distances (Å)

The primes denote the inversions at the origin. The  $\sigma_L$  are the e.s.d.'s of the least-squares results.

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	300° K	240° K	110° K	r(300° K)-
				r(110°K)
$O(1) \cdots C(4, -b)$	3.253	3.216	3.159	0.094
$O(1) \cdots C(5', +a)$	3.366	3.352	3.319	0.047
$O(1) \cdots C(4, -b-c)$	3.479	3.479	3.440	0.039
$O(1) \cdots C(5', +a+c)$	3.568	3.551	3.502	0.066
$N(1) \cdots C(1, +c)$	3.471	3.439	3.381	0.090
$N(1) \cdots C(4, +c)$	3.527	3.515	3.470	0.057
$N(1) \cdots C(3', +c)$	3.594	3.547	3.479	0.115
$C(5) \cdots C(5', +a+b+c)$	3.514	3.491	3.461	0.023
$C(2) \cdots C(3, +c)$	3.542	3.512	3.451	0.091
$C(4) \cdots C(5', +a+b+c)$	3.582	3.567	3.540	0.042
$C(1) \cdots C(2', +c)$	3.689	3.649	3.580	0.109
$C(1) \cdots C(1', +c)$	3.728	3.682	3.617	0.111
$O(1) \cdots H(4', +a)$	2.55	2.54	2.51	0.04
$O(1) \cdots H(3, -b-c)$	2.60	2.54	2.53	0.02
$O(1) \cdots H(5', +a+c)$	<b>2</b> ·73	<b>2·</b> 71	2.66	0.07
$O(1) \cdots H(2, -b)$	2.76	2.76	2.73	0.03
$N(1)\cdots H(2,+c)$	2.63	2.64	2.61	0.02
$C(4) \cdots H(2, +c)$	2.92	2.94	2.90	0.02
$C(5)\cdots H(2,+c)$	3.03	3.04	2.99	0.04
$C(4) \cdots H(5', +a+b+c)$	3.05	3.04	3.01	0.04
$C(4) \cdots H(3', +b+c)$	3.12	3.08	3.03	0.09
$C(5) \cdots H(5, -c)$	3.14	3.18	3.10	0.04
$H(4) \cdots H(5, -c)$	2.44	2·47	2.43	0.01
$H(2) \cdots H(3, -c)$	2.52	2.50	2.49	0.03
$\mathbf{H}(3)\cdots\mathbf{H}(3',+b+c)$	<b>2</b> ·57	<b>2</b> ·55	2.51	0.06
$H(2) \cdots H(5, -c)$	2.63	<b>2</b> ·71	2.64	-0.01
$H(1)\cdots H(1', +a+c)$	<b>2·6</b> 7	2.62	2.53	0.14
$\sigma_L(\text{non-H})$	0.005	0.004	0·00 <b>3</b>	
$\sigma_L$ (one H)	0.03	0.05	0.02	
$\sigma_L(H-H)$	0.04	0.03	0.03	

### Molecular structure

The bond distances and angles are given in Tables 5 and 6, respectively. Rigid-body librational corrections were applied by the method of Cruickshank (1961) using appropriate Gaussian-breadth parameters (Ito, Minobe & Sakurai, 1970). As can be seen from the Tables, the molecular dimensions are almost constant at the different temperatures; the average values with standard deviations are given in the last columns of the Tables and are also shown in Fig. 3.

The three-membered ring of the ethyleneimino group is approximately a regular triangle with bond angles of 61.2, 59.2 and 59.6°. The two N–C distances within the ring (1.475 and 1.469 Å) agree with the normal



Fig. 3. Average bond distances (Å) and angles (°) of ethyleneimine quinone.

# Table 5. Bond distances (Å)

The figures in parentheses are the librational corrections (positive). The  $\sigma_L$  in the lowest lines are the e.s.d.'s of the least-squares results. The  $\sigma$  in the last column are the composites of  $\sigma_L$  and the e.s.d.'s of the three sets of results.

	300° K	240° K	110° K	Average	σ
O(1) - C(3)	1.225 (1)	1.222(1)	1.225 (0)	1.224	0.003
N(1) - C(1)	1.379 (1)	1.387 (1)	1.383 (1)	1.383	0.004
N(1) - C(4)	1.477 (3)	1.472 (3)	1.477 (1)	1.475	0.003
N(1)-C(5)	1.472 (3)	1.466 (3)	1.470 (1)	1.469	0.004
C(1) - C(2)	1.343 (4)	1.347 (2)	1.351 (1)	1.347	0.004
C(1) - C(3')	1.520 (5)	1.517 (4)	1.510(1)	1.516	0.004
C(2) - C(3)	1.448 (2)	1.460 (2)	1.456 (1)	1.455	0.002
C(4) - C(5)	1.494 (4)	1.499 (4)	1.500 (2)	1.498	0.004
C(2) - H(1)	0.95	0.97	0.98	0.97	0.02
C(4) - H(2)	1.05	1.03	1.01	1.03	0.02
C(4) - H(3)	0.93	0.98	0.96	0.96	0.03
C(5) - H(4)	1.04	1.02	0.99	1.02	0.03
C(5) - H(5)	1.02	0.98	1.00	1.00	0.02
$\sigma_L(\text{non-H})$	0.004	0.003	0.002	0.003	
$\sigma_L$ (C–H)	0.03	0.05	0.05	0.02	

## Table 6. Bond angles (°)

The librational corrections are not indicated because they were small (less than  $\pm 0.1$ ). The  $\sigma_L$  are the e.s.d.'s of the least-squares results. The  $\sigma$  are the composites of  $\sigma_L$  and the e.s.d.'s of the three sets of results.

	300° K	240° K	110° K	Average	$\sigma$
C(1) - N(1) - C(4)	121.3	120.7	120.9	121.0	0.3
C(1) - N(1) - C(5)	120.8	120.6	120.5	120.6	0.5
C(4) - N(1) - C(5)	60.9	61.4	61.2	61.2	0.3
N(1)-C(1)-C(2)	124.3	124.1	124.1	124-2	0.5
N(1)-C(1)-C(3')	116-1	115.7	115.5	115.8	0.3
C(2) - C(1) - C(3')	119-4	120.0	120.2	119.9	0.3
C(1) - C(2) - C(3)	123.0	122.5	122.2	122.6	0.3
C(1) - C(2) - H(1)	122	123	121	122	1
C(3) - C(2) - H(1)	115	115	117	116	1
O(1) - C(3) - C(1')	119.7	120.4	120.4	120.2	0.3
O(1) - C(3) - C(2)	122.7	122.1	122.0	122-3	0.3
C(2) - C(3) - C(1')	117.6	117.5	117.6	117.6	0.5
N(1)-C(4)-C(5)	59.4	59.1	59.2	59·2	0.5
N(1)-C(4)-H(2)	118	116	116	117	1
N(1)-C(4)-H(3)	116	115	116	116	1
C(5) - C(4) - H(2)	117	118	118	118	1
C(5) - C(4) - H(3)	124	120	121	122	2
H(2)-C(4)-H(3)	113	116	115	115	2
N(1)-C(5)-C(4)	59.7	59.5	59.6	59.6	0.5
N(1)-C(5)-H(4)	116	116	117	116	1
N(1)-C(5)-H(5)	113	115	115	114	1
C(4) - C(5) - H(4)	117	116	118	117	1
C(4) - C(5) - H(5)	118	122	120	120	2
H(4)-C(5)-H(5)	119	116	115	117	2
$\sigma_L(\text{non-H})$	0.3	0.5	0.1	0.5	
$\sigma_L$ (one H)	2	1	1	1	
$\sigma_L$ (two H)	3	2	2	2	

N-C single-bond distance (1.47 Å), whereas the C-C distance (1.498 Å) is significantly shorter than the single-bond distance (1.54 Å) (Pauling, 1960). These distances may also be compared with those of a free ethyleneimine molecule, N-C=1.488 and C-C=1.480 Å, determined by microwave spectroscopy (Turner, Fiora & Kendrick, 1955); the N-C and C-C distances of ethyleneimine quinone are 0.016 Å shorter and 0.018 Å longer, respectively, than those of the

ethyleneimine molecule. The H–C–H planes are approximately perpendicular (average  $87.7^{\circ}$ ) to the threemembered ring. The observed H–C–H angles, 115 (2) and 117 (2)°, are significantly larger than the tetrahedral angle and are in good agreement with the theoretical prediction of 116° for cyclopropane (Coulson & Mof-fitt, 1949).

The observed dimensions of the quinone ring in ethyleneimine quinone are quite similar to those in similar crystals; for example, in chloranilic acid and chloranilic acid anhydrate, the average bond distances are: C=O=1.225, C=C=1.346, C-C=1.506 and 1.446 Å (Anderson, 1967). It should be noted that the two C-C single-bond distances within a quinone ring in these crystals are significantly different; the differences are 0.061 and 0.060 Å in ethyleneimine quinone and chloranilic acid, respectively. However, in pbenzoquinone (Trotter, 1960) or in symmetrically substituted quinones such as tetrachloro-*p*-benzoquinone (Chu et al., 1962), the two C-C distances are almost the same. As was pointed out by Anderson (1967) for chloranilic acid, this asymmetry of the C-C distances together with the short N(1)-C(1) distance (1.383 Å) shows that the following canonical forms are also important in ethyleneimine quinone:



The equations of the best-fit planes through the quinone rings are given by:

-0.4452x - 0.4019y + 0.8967z = 0 (300°K)	)
-0.4457x - 0.4012y + 0.8906z = 0 (240°K	)
-0.4487x - 0.3991y + 0.8865z = 0 (110°K)	)

where x, y and z are measured along the crystallographic cell edges in Å units. The maximum deviation of the ring carbon atoms is 0.051 Å. The oxygen and nitrogen atoms also lie approximately on these planes; the average deviations are 0.042 and 0.082 Å, respectively.

# Bonding electrons and the bent bond

The equations of the ethyleneimino planes are given by:

- -0.1266x + 0.3742y + 0.8936z = 2.174 (300 ° K)-0.1328x + 0.3844y + 0.8930z = 2.193 (240 ° K)
- -0.1346x + 0.3867y + 0.8947z = 2.190 (110°K).

Difference electron density maps in these planes at the three temperatures are shown in Fig. 4. Although the peak values (from +0.06 to +0.26 eÅ<sup>-3</sup>) and peak positions are slightly different for different temperatures, three residual peaks always appear outside the triangle and approximately at the middle of each side.

If  $\sigma(F_o)$  is assumed to be  $KF_o$  with K constant, the standard deviation of the electron density can be estimated from the equation

$$\sigma(\varrho) = K \left(\frac{p}{2\pi}\right)^{3/4} \left(\frac{1}{V} \sum Z^2\right)^{1/2}$$

where Z is the atomic number, V is the unit-cell volume, and p depends on the shape of the atom including the thermal vibration. With K=4%, and p=4, 3 and 2 for each temperature,  $\sigma(\varrho)$  is 0.05, 0.04 and 0.03 eÅ<sup>-3</sup> at 300, 240 and 110°K. Since the majority of the residual peaks are more than twice these standard deviations, and also appear systematically at the different temperatures, they can be attributed to bonding electrons. The peaks are displaced from the sides of the triangles by 0.33 Å (average). The line joining a peak to each of the adjacent atoms is inclined 24° (average) to the internuclear line. Therefore, if we assume that the bond is directed from an atom to the adjacent residual peaks, the 'bent bond' is 108° instead of the highly strained angle of 60°.

These results are in fairly good agreement with those for *cis*-1,2,3-tricyanocyclopropane; the corresponding displacement and inclination angle are 0.32 Å and 22° respectively (Hartman & Hirshfeld, 1966). The result for tetracyanoethylene oxide (Matthews & Stucky, 1970) is not quite in agreement with the present result. In the ethylene oxide ring, although the residual electron density of about 0.45 e Å<sup>-3</sup> appears at the outside of the C-C bond, the bend in the C-O bond is obscured by the tail off of the broad maximum near the centre of the ring. Such an accumulation of electron density at the centre of the ring is not observed in the ethyleneimine molecule.

Difference electron density maps through the quinone rings at the three temperatures are shown in Fig. 5. Residual peaks are observed on almost all internuclear lines. They are more pronounced with decreasing temperatures. In the plane of the ring, the peaks on the  $\pi$ -bonds are systematically lower than those of the  $\sigma$ -bonds. On the C=O double bond, there are no well-defined peaks; similar absence is also observed in 2,5-dimethyl-*p*-benzoquinone (Hirshfeld & Rabinovich, 1967), and in fumaramic acid (Hirshfeld, 1971).

### Thermal vibrations

As can be seen from Table 2 and the last column of Table 1, the temperature factors of the atoms decrease systematically with decreasing temperatures. The mean-square amplitudes along the  $c^*$  direction  $(U_{33})$  are

significantly larger than those along the  $a^*$  and  $b^*$  directions ( $U_{11}$  and  $U_{22}$ ); *i.e.* the atoms vibrate more out of the molecular sheet than within the sheet. This anisotropy of vibration is reflected on the anisotropy of thermal expansion of the crystal; the linear expansion coefficients within the range 300 to  $110^{\circ}$ K along

the **a**, **b** and **c** directions are 61, 45 and  $92 \times 10^{-6}$ , respectively.

The anisotropic temperature factors of the atoms were transformed into the rigid-body vibration of the molecule by the method of Cruickshank (1956). The axes of molecular vibration were taken along the



Fig. 4. Difference electron density maps in the plane of the ethyleneimino group at (a)  $300^{\circ}$ K, (b)  $240^{\circ}$ K and (c)  $110^{\circ}$ K. Contour lines are drawn with the interval of 0.05 eA<sup>-3</sup>.

principal axes of the moment of inertia as shown in Fig. 6. The most probable values of the translational and librational tensors,  $T_{ij}$  and  $\Omega_{ij}$  respectively, are given in Table 7. All non-hydrogen atoms were used for the calculations. The observed and calculated temperature factors of the individual atoms were in fairly

good agreement; the average relative errors at 300, 240 and  $110^{\circ}$ K are 9.7, 8.1 and  $11.0^{\circ}$ K respectively. It should be noted that as the temperature goes down from 300 to  $110^{\circ}$ K, the root-mean-square amplitudes of the translational and librational vibrations decrease to about one half of the original.



Fig. 5. Difference electron density maps in the plane of the quinone ring at (a)  $300^{\circ}$ K, (b)  $240^{\circ}$ K and (c)  $110^{\circ}$ K.



Fig. 6. Axes of the rigid-body vibration. Axis 3 is out of the plane of the paper.

 Table 7. Tensors of the rigid-body vibration and the root-mean-square amplitudes of vibration along the principal axes of the tensors

The principal axes of the vibrational tensors, 1', 2', 3' and 1'', 2'', 3'', are approximately parallel to those of the moment of inertia, 1, 2, 3, respectively.

	300° K	240° K	110° K
$T_{11} (10^{-4} \text{ Å}^2)$	284 (8)	196 (5)	88 (3)
T <sub>22</sub>	250 (10)	195 (7)	90 (4)
T <sub>33</sub>	281 (15)	185 (9)	77 (5)
$T_{12}$	0 (8)	0 (5)	2 (3)
$T_{13}$	49 (8)	18 (5)	8 (3)
$T_{23}$	-3 (11)	-3(7)	-4 (4)
t(1') Å	0.182	0.145	0.096
t(2')	0.158	0.140	0.092
t(3')	0.153	0.131	0.082
$\Omega_{11} \left[ 10^{-1}  (^{\circ})^2 \right]$	267 (17)	209 (11)	68 (6)
$\Omega_{22}$	46 (5)	28 (3)	11 (2)
$\Omega_{33}$	40 (5)	34 (3)	11 (1)
$\Omega_{12}$	-10 (7)	5 (4)	3 (2)
$\Omega_{13}$	8 (8)	3 (5)	1 (3)
$\Omega_{23}$	-2 (4)	3 (3)	1 (2)
ω(1″) (°)	5.2	4.6	2.6
$\omega(2^{\prime\prime})$	2.1	1.6	1.0
$\omega(3^{\prime\prime})$	2.0	1.9	1.1

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Fukuhara, 1967). This work was supported, in part, by the Science Research Grant of the Ministry of Education.

## References

ANDERSON, E. K. (1967). Acta Cryst. 22, 188-191.

- BECKA, L. N. & CRUICKSHANK, D. W. J. (1963). Proc. Roy. Soc. A 273, 435–454.
- BONACCORSI, R., SCROCCO, E. & TOMASI, J. (1970). J. Chem. Phys. 52, 5270–5284.
- CHU, S. S. C., JEFFREY, G. A. & SAKURAI, T. (1962). Acta Cryst. 15, 661–671.
- Coulson, C. A. & Moffitt, W. E. (1949). *Phil. Mag.* 40, 1–35.
- CRUICKSHANK, D. W. J. (1956). Acta Cryst. 9, 754-756.
- CRUICKSHANK, D. W. J. (1961). Acta Cryst. 14, 896-897.
- FRITCHIE, C. J. JR (1966). Acta Cryst. 20, 27-36.
- GAUSS, W. & PETERSEN, S. (1955). Angew. Chem. 67, 217-231.
- HAMILTON, W. C. (1959). Acta Cryst. 12, 609-610.
- HARTMAN, A. & HIRSHFELD, F. L. (1966). Acta Cryst. 20, 80–82.
- HIRSHFELD, F. L. (1971). Acta Cryst. B27, 769-781.
- HIRSHFELD, F. L. & RABINOVICH, D. (1967). Acta Cryst. 23, 989–1000.
- Howells, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). Acta Cryst. 3, 210-214.
- International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
- ITO, T. (1971). Rep. Inst. Phys. Chem. Res. 47, 47-60.
- ITO, T., MINOBE, M. & SAKURAI, T. (1970). Acta Cryst. B26, 1145–1151.
- ITO, T. & SAKURAI, T. (1972). Acta Cryst. A28, S11.
- KOCHANSKI, E. & LEHN, J. M. (1969). Theoret. Chim. Acta 14, 281-304.
- LIPSON, H. & COCHRAN, W. (1953). The Determination of Crystal Structures, p. 288. London: Bell.
- MATTHEWS, D. A. & STUCKY, G. D. (1971). J. Amer. Chem. Soc. 93, 5954–5959.
- PAULING, L. (1960). The Nature of the Chemical Bond. Ithaca: Cornell Univ. Press.
- SAKURAI, T., ITO, T. & IIMURA, Y. (1970). Rep. Inst. Phys. Chem. Res. 46, 82–99.
- SAKURAI, T., ITO, T., IWASAKI, H., WATANABE, Y. & FUKU-HARA, M. (1967). *Rep. Inst. Phys. Chem. Res.* 43, 62–69.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.
- TROTTER, J. (1960). Acta Cryst. 13, 86-95.
- TURNER, T. E., FIORA, V. C. & KENDRICK, W. M. (1955). J. Chem. Phys. 23, 1966.